

Gelling by Heating

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We introduce a simple model, a binary mixture of patchy particles, which has been designed to form a gel upon heating. Due to the specific nature of the particle interactions, notably the number and geometry of the patches as well as their interaction energies, the system is a fluid both at high and at low temperatures T , whereas at intermediate T s the system forms a solid-like disordered open network structure, i.e. a gel. Using molecular dynamics we investigate the static and dynamic properties of this system.

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Some of the most versatile and efficient strategies for designing new materials with unconventional behavior are based on the idea of *competitive interaction*. While in biology the term *competitive interaction* indicates the result of rivalry between two or more species competing for resources, in physics it stands for the presence of several interaction mechanisms that can stabilize competing local structures, leading to novel and highly interesting features of the system. Recent examples for this mechanism in soft matter systems include, among others, the competition between short-range attraction and long-range repulsion in charged colloids giving rise to cluster phases [1–3], the competition between chaining and branching in patchy colloids [4, 5] where a specific design of the inter-patch interactions results in a phase diagram in which the density of the coexisting liquid approaches the density of the gas [5], and the design of DNA-coated colloids with two different DNA sequences for the purpose of establishing a competition between intra and inter-particle interactions, favoring crystal formation [6]. Often the very nature of these competing mechanisms promotes the emergence of a structure controlled by energy (stable at low T) which competes with a structure stabilized by entropy at intermediate T .

Recent progress in the synthesis of colloids have led to a new generation of particles with highly directional and selective interactions, providing valence to colloids [7]. The ability to tune the interactions between nano- and meso-sized particles almost at will [8, 9], and to design the geometric properties of the patches [10] and/or their functionalization, offers today the possibility to exploit the idea of competitive interactions to modulate material properties with external control parameters. In this Letter we develop one such possibility: The design of a material whose viscosity increases upon heating. In particular, we show how a simple design of a binary mixture of limited valence particles can indeed provide a model where the competition between entropy and potential energy causes the system to show a re-entrant behavior, passing reversibly from a fluid to a gel and again to a fluid when T is varied.

It has been shown that patchy colloidal particles with a limited number f of attractive patches progressively

cluster when cooled, leading such system to form a percolating network that at sufficiently low T will incorporate all particles in the system [11–16]. During this process, the diffusion coefficient progressively decreases and the viscosity simultaneously increases. In the network state the lifetime of the bonds (a T -controlled quantity) fixes the timescale over which the system behaves as a solid. It is known that when $f = 4$, the particles (here called A species) form a random tetrahedral network which closely resembles the structure of network-forming atomic systems like silica and silicon [17]. To melt the network at low T , we consider the addition of a second species (B) with a single bonding patch that competes for bonding with the patches on the network forming A -species. The idea is to design a competitive mechanism such that the bonding between A - and B -particles becomes dominant, *but only* at a temperature much lower than the one at which the AA -network is formed. As a result, the stable low- T phase consists of A -particles decorated with f B -particles which are free to diffuse in the sample volume, whereas at intermediate T the system forms a highly viscous AA -network that is progressively fragmented and transformed into a fluid upon heating.

Model: We consider a binary mixture of patchy colloids where each A -particle has $f = 4$ patches on its surface that are arranged in a tetrahedral geometry and the B -particles have only one patch (see Fig. 1). The patch-patch interaction is modeled via a Kern-Frenkel potential [18], a model that has been extensively used over the last decade to compare simulations and experiments on the self-assembly of patchy colloids [19–21]. Each A -patch can interact either with a B -patch with unit energy ϵ_{AB} and bonding volume \mathcal{V}_{AB} or with another A -patch with energy $\epsilon_{AA} = 0.95\epsilon_{AB}$ and $\mathcal{V}_{AA} (\gg \mathcal{V}_{AB})$. No BB -bonding is allowed. The bonding volumes are each determined by an interaction range δ_α and an angular patch width θ_α ($\alpha \in \{AA, AB\}$) (see Fig. 1 and Ref. [22]). The attractive patch-patch interaction is complemented by an isotropic hard-core repulsion, where the spherical cores have diameters σ_A and $\sigma_B = 0.35\sigma_A$. The size ratio was chosen such that the B -particles can block the A -patches from bonding to other A -patches without significantly increasing the packing fraction of the pure A

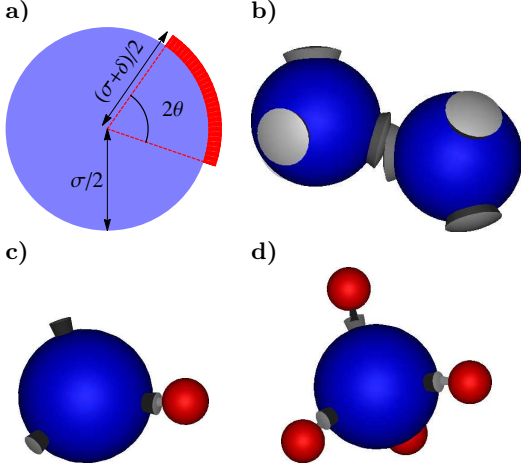


FIG. 1. a) Schematic of the interaction parameters in the Kern-Frenkel model. An A -patch can bond with either another A -particle (b), or with a B -particle (c). Panel (d) shows a “flower”, i.e. a fully bonded cluster consisting of one A -particle and four B -particles, representing the lowest-energy state of the system. Here the interaction ranges and the angular patch widths are $\cos \theta_{AA} = 0.92$, $\delta_{AA} = 0.15\sigma_A$, and $\cos \theta_{AB} = 0.99$, $\delta_{AB} = 0.2\sigma_A$. With these choices $\mathcal{V}_{AA} = 3.49 \cdot 10^{-3}\sigma_A^3$ and $\mathcal{V}_{AB} = 3.79 \cdot 10^{-5}\sigma_A^3$ [22]. Note that in the binary Kern-Frenkel model, θ and δ of each bond are defined by the species of *both* bonding partners and are not properties of individual particles.

system. Due to geometric constraints, each patch can be involved in only a single bond.

Using event-driven molecular dynamics simulations [22–25], we have studied a system of $N_A = 600$ and $N_B = 2400$ particles, corresponding to a total number density $\rho\sigma_A^3 = 3.0$, with partial number densities $\rho_A\sigma_A^3 = 0.6$ and $\rho_B\sigma_A^3 = 2.4$, for a wide range of T , whose unit is given by ϵ_{AB}/k_B , where k_B is Boltzmann’s constant. The composition of the system is thus fixed at $x_A = 0.2$. The density $\rho_A\sigma_A^3 = 0.6$ of A -particles corresponds to the optimal density at which tetrahedral particles form an unstrained fully bonded network[26]. With this composition, the fully bonded network has an energy of $2N_A\epsilon_{AA}$, whereas a configuration in which all the B -particles are bonded to the A -particles has a significantly lower energy of $4N_A\epsilon_{AB}$. We also simulate for a low T ($= 0.04\epsilon_{AB}/k_B$) a reference system composed of 600 *flowers* (see Fig. 1d), i.e. A -particles bonded to four B -particles. At this low T no bond breaking events take place within the simulation time.

Results: Figure 2 demonstrates the basic mechanism of the competitive interactions present in our system. It shows the probability that a patch on an A -particle is bonded to another A -patch (p_{AA}) or to a B -patch (p_{AB}) as a function of the inverse T . On cooling, p_{AA} starts to grow, signaling the onset of the network formation, reaching a maximum around $T = 0.11\epsilon_{AB}/k_B$. We recall that within a mean-field description, percolation of par-

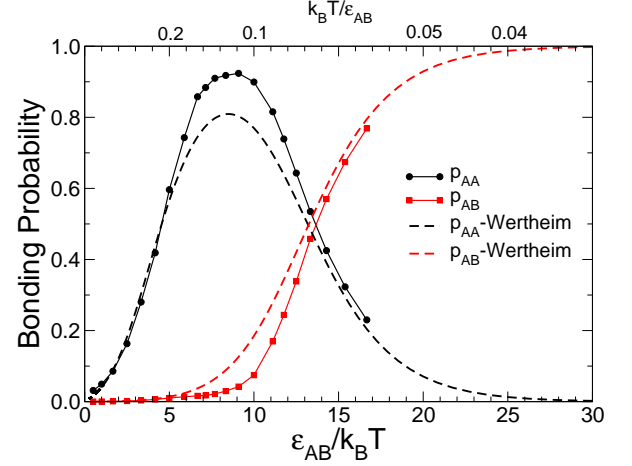


FIG. 2. Probability that a patch on an A -particle is bonded to another patch on an A -particle, p_{AA} (black circles), or to a patch on a B -particle, p_{AB} (red squares). The dashed lines are the prediction for these probabilities as obtained from the Wertheim theory.

ticles with valence $f = 4$ takes place at $p_{AA} = 1/3$ [27]. Since at the maximum we find $p_{AA} \approx 0.9$ we can conclude that at this T the A -particles have formed a highly bonded percolating network. Upon further cooling, p_{AB} significantly increases, showing that the AB -bonds are starting to replace the AA ones, i.e. while p_{AB} approaches 1.0, $p_{AA} \rightarrow 0$. The entropy associated with the larger bonding volume \mathcal{V}_{AA} for the AA interaction is crucial for promoting the formation of a large number of AA -bonds at intermediate T , before the energetically preferred but entropically disfavored AB -bonds set in. Fig. 2 also shows the parameter-free theoretical predictions for the bonding probabilities as obtained from the first-order thermodynamic perturbation theory developed by Wertheim [28–30] (details on the Wertheim calculations are reported in [22]). The Wertheim theory nicely captures the mechanism of competing interactions, reproducing the position and height of the maximum of p_{AA} as well as the low T trends of p_{AA} and p_{AB} .

Figure 3 shows the unusual T dependence of the structure of the system, which also reflects the non-monotonic behavior of p_{AA} . At high T , the partial structure factor $S_{AA}(q)$ shows the conventional q -dependence found in simple liquids with a main peak around $q\sigma_A = 7.2$. Upon decreasing T the main peak splits into two, one located around $q\sigma_A = 5.2$ and a higher one around 8.4. This double peak feature is typical of liquids that have a local tetrahedral network structure, such as silicon or silica [17]. The peak at $q\sigma_A \approx 8.4$ corresponds to the nearest neighbor distance between two bonded A -particles, whereas the one placed around 5.2 is associated with the second-nearest neighbors in the tetrahedral network. Note that this double peak structure is most pronounced at $T \approx 0.11\epsilon_{AB}/k_B$, i.e. at the T at which p_{AA} has a maximum (see Fig. 2) and hence the gel is maximally

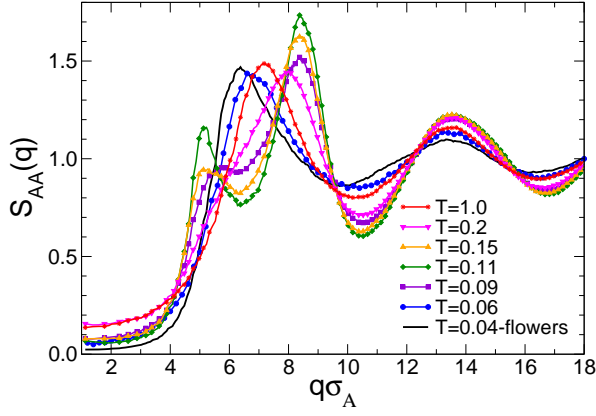


FIG. 3. Partial structure factor $S_{AA}(q)$ for different values of T (solid lines with different symbols). The $S_{AA}(q)$ for a fluid of flowers at $T = 0.04\epsilon_{AB}/k_B$ (black solid line) is also represented.

connected. When T is lowered even further the double peak structure disappears and $S_{AA}(q)$ becomes again similar to the structure factor of a fluid composed of flowers (which is also included in Fig. 3 as a reference). Since the size of a flower is larger than that of an A -particle, the peak position at low T is to the left of the one observed at high T .

We now quantify the effect of the competing interactions on the dynamics of the system and provide evidence that the change of the structure rich in AB -bonds at low T to the highly bonded AA -network generates a slowing down of the dynamics on heating. To do this, we calculate the mean squared displacement (MSD) for the particles of both species and then their corresponding diffusion coefficients D_α ($\alpha \in \{A, B\}$) from the long-time behavior of the MSD via the Einstein relation [31]. To subtract the trivial trend originated from the T -dependence of the thermal velocity we divide D_α by a reference diffusion coefficient $D_0 \equiv \sigma_A^2/\tau_0$, where $\tau_0 = \sqrt{m_A \sigma_A^2/k_B T}$ and m_A is the mass of an A -particle.

Figure 4 shows the T -dependence of D_α in an Arrhenius plot. At high T , D_α is approximately constant for both type of particles, indicating that bonds do not play a significant role. On cooling, D_A starts to decrease very rapidly, with a super-Arrhenius T -dependence reminiscent of that observed in molecular networks [17], turning into an Arrhenius law with an activation energy approximately equal to $2\epsilon_{AA}$ (see dashed line in Fig. 4). Similar values of the activation energy are typically found in tetrahedral network-forming systems where most of the particles belong to the percolating cluster, and bond breaking is the bottleneck for relaxation [15, 32, 33]. Before the gel starts to decompose at a temperature below $T \approx 0.11\epsilon_{AB}/k_B$, D_A has already decreased by four orders of magnitude compared to its value at high T , indicating the formation of a persistent network. For $T \lesssim 0.11\epsilon_{AB}/k_B$, D_A starts to increase. This rising persists down to the lowest T at which we were able to equilibrate the system.

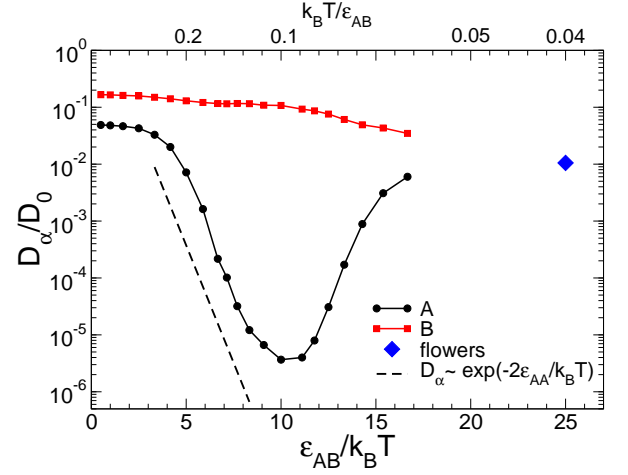


FIG. 4. Arrhenius plot of the normalized diffusion coefficient D_α/D_0 ($\alpha = A$, circles, $\alpha = B$, squares). Also included is an Arrhenius law with activation energy $2\epsilon_{AA}$ (dashed line). The diffusion coefficient of a fluid of flowers at low T is represented by a blue diamond.

brating the system. We emphasize that this non-monotonic T -dependence is only observed for the A -particles, i.e. the particles which are involved in the formation of the network. In contrast, D_B shows only a rather mild T -dependence. Figure 4 also shows the diffusion coefficient of the fluid of flowers at $T = 0.04\epsilon_{AB}/k_B$ for which $D_A = D_B$. This common value of the diffusion coefficient provides a low- T limit to which both D_A and D_B converge, consistent with the trends shown by D_A and D_B at low T .

A non-monotonic behavior of the characteristic time is also found in the time evolution of the collective- and self-intermediate scattering functions. Their study provides insight into how the relaxation dynamics depends on the considered length scale. Figure 5a shows an Arrhenius plot of the relaxation time $\tau_A(q)$ determined from the time integral of the intermediate scattering function of the A -particles for two different q -vectors: $q\sigma_A = 5.2$ and $q\sigma_A = 7.2$, which correspond, respectively, to the location of the first peak in the network and in the high- T fluid (see Fig. 3). We find that the self and collective relaxation times $\tau_A(q)$, normalized by τ_0 , show qualitatively the same T -dependence: a plateau at high T , a fast increase within the T -range in which the network is formed, a quick decrease once the network starts to break up again, and a final plateau at low T . This T -dependence is observed for both values of q , indicating that the relaxation mechanism does not depend on the length scale considered. Analogous to the diffusion coefficient, the self and collective dynamics of the B -particles are found to be faster than those of the A -particles and their q and T dependence will be reported elsewhere.

To provide further evidence that the system is ergodic on long time scales, i.e. that the structure of the system has completely lost its memory of the initial state, we

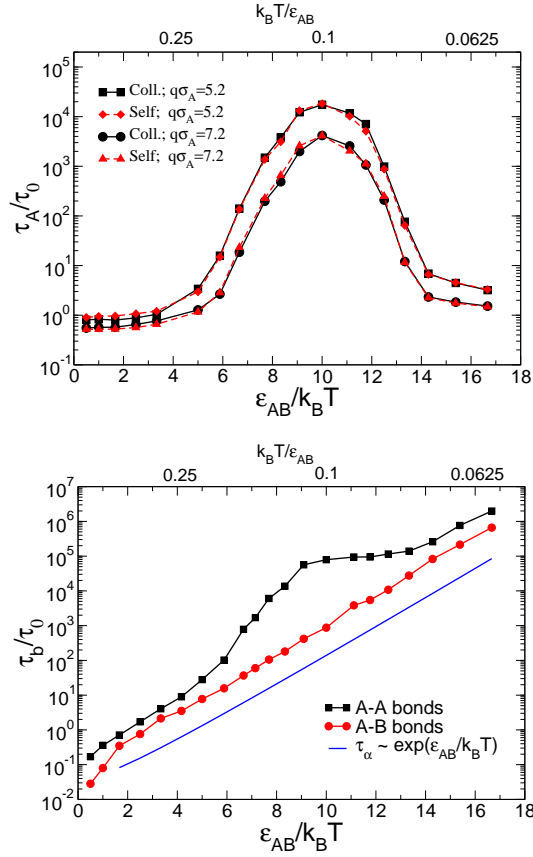


FIG. 5. a) Arrhenius plot of the normalized relaxation time $\tau_A(q)/\tau_0$ as obtained from the self (dashed lines) and collective (solid lines) scattering functions, where $\tau_0 = \sqrt{m_A \sigma_A^2 / k_B T}$. The different curves correspond to the wave-vectors given by the first two peaks in $S_{AA}(q)$. b) Arrhenius plot of the normalized bond-persistence time τ_b/τ_0 for the AA (squares) and AB bonds (circles). Also included is an Arrhenius law with activation energy ϵ_{AB} (blue solid line).

investigate the bond persistence function $p_b(t)$, i.e. the probability that a bond which is present at time zero is also present at time t . When $p_b(t)$ approaches zero, all bonds which were present at time zero have been broken. Hence, the relaxation time of $p_b(t)$ provides information on the restructuring time of the network connectivity. Figure 5b shows an Arrhenius plot with the T -dependence of the decay time τ_b , where $p_b(\tau_b) = e^{-1}$. At intermediate and low T , τ_b is larger than the relaxation times shown in Fig. 5a. We find thus that $p_b(t)$ decays to zero only on a time scale that is significantly longer than the relaxation times associated with the scattering functions, confirming that some fraction of spatial decorrelation of the network, as quantified by the collective scattering function, takes place at partially fixed bonding pattern. In other words, while the decay to zero of the scattering functions for a given q -value implies that the particles have moved over a distance on the or-

der of $2\pi/q$, such motion does, however, not necessarily require that *all* bonds are broken, since, e.g., a cluster of particles can move in a collective manner. A bond can persist up to very long times even if the structure of the system changes significantly. The extreme case occurs at very low T where the system is a fluid of flowers that relaxes relatively quickly but in which AB -bonds survive for a very long time. Figure 5b also shows the different T -dependence of the lifetime of the AA - and of the AB -bonds. An Arrhenius dependence with an activation energy very close to ϵ_{AB} (see dashed line in Fig. 5b) characterizes the AB -bonds in the entire T -range, suggesting that the mechanism for the breaking of an AB -bond is not collective in nature but a simple activated process. In contrast to this behavior, the breaking time for an AA -bond follows an Arrhenius law at high T but becomes super-Arrhenius within the T -region in which the gel forms, showing that the bond-breaking process becomes coupled to the degree of bonding. At low T , when most of the A -sites are bonded to B -particles and the network is disrupted, the effective activation energy decreases again to recover at very low T an Arrhenius behavior with an activation energy given by ϵ_{AA} .

Conclusions: In summary, we have shown that a judicious choice of the interaction parameters of a binary mixture of A and B patchy particles allows us to generate a non-monotonic T -dependence of its dynamic properties. Essentially, we set up a competition between network-forming AA -bonds and network-breaking AB -bonds, and tune the balance between both bond types by choosing their bonding volumes (and therefore the entropy) and energies. At high T , very few bonds are formed, and the system behaves similar to a binary fluid of hard spheres. At slightly lower T , the stability of a stiff, percolating network is ensured by the larger entropy associated with the much larger bonding volume \mathcal{V}_{AA} . However, when T is decreased even further, the system instead forms a fluid of small clusters, stabilized by a much larger number of AB -bonds, corresponding to a lower potential energy. We have shown that, compared to both the high- T and low- T fluids, the network state relaxes and diffuses more slowly by several orders of magnitude. Thus, the system forms a reversible gel that transforms into a fluid upon both heating and cooling. We conclude by listing two experimental systems which we believe are very promising candidates to experimentally test the ideas presented in this Letter: a solution of DNA constructs of valence four[34, 35] in the presence of competing DNA single strands and the binary mixture of patchy particles recently synthesized[9]. Both these model systems have the potential to provide soft materials that gel on heating.

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